APPENDIX A

PCB ENVIRONMENTAL FATE AND EFFECTS

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APPENDIX A

PCB ENVIRONMENTAL FATE AND EFFECTS

Because PCBs are the compounds of greatest concern in the area of the Housatonic River under study, they will be the focus of this discussion. However, it is possible that other chemicals, such as dioxins/furans, will warrant evaluation as well; the modeling concepts discussed below are equally applicable to all hydrophobic, and in particular, bioaccumulative contaminants.

PCB CLASSIFICATION AND PHYSICAL/CHEMICAL PROPERTIES

Polychlorinated biphenyls (PCBs) are synthetic organochlorine chemicals of 12 carbon atoms, with chlorine atoms substituted for hydrogen atoms in any of the 10 numbered positions, as shown in (**Figure 1**). The positions can be referred to by name, with four *ortho* positions, four *meta* positions, and two *para* positions. Positions occupied by chlorine atoms can be indicated, for example as 2,4' or by the nonstandard but more convenient notation 2/4, which indicates the bilateral structure more readily. The latter convention will be used in this appendix.
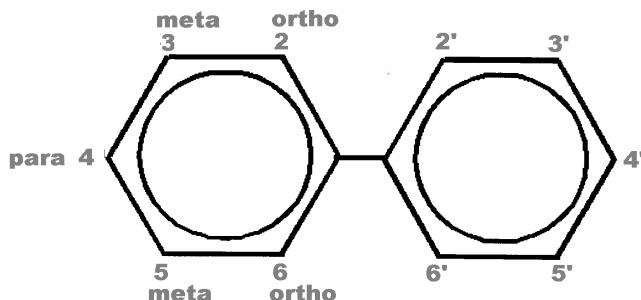

Figure 1   Structure and Nomenclature of PCBs

PCBs can be classified into level-of-chlorination homolog groups, which are groups of PCB congeners having the same number of chlorine substitutions. Level of chlorination affects various physicochemical properties of the PCB molecule such as the octanol/water partition coefficient (K_{ow}), solubility, vapor pressure, and Henry's Law constant, which in turn affect processes such as volatilization, and loss from water, sediments, and floodplain soils. Similarly, level of chlorination also controls (in part) biologically mediated processes such as biotransformation, uptake, and accumulation (Schweitzer et al., 1997). Although there is still a range of variation within a homolog group, in general PCB congeners with similar levels of chlorination tend to share similarities with regard to these properties and processes. K_{ow}, in particular, generally increases with increasing level of chlorination and is a major controlling variable affecting the lipophilic behavior of PCBs, with increased chlorine substitution usually resulting in a higher K_{ow} and consequent elevated affinity for lipids. The relationship between certain physical constants and PCB homolog group is shown for a number of PCB congeners in Table 1.

Table 1

Examples of Structure and Physical/Chemical Properties of PCBs

Homolog	IUPAC No.	Structure	Aroclor 1254 wt. %	Aroclor 1260 wt. %	Toxicity TEF	Molecular Weight g/mol	Solubility g/m^3	V Press Pa	Henry's Law X 10^4 atm m^3/mol	log K$_{OW}$
Mono CBP			0	0		189	7.2	2.3		4.47
	1	2							7.38	4.601
	2	3							4.88	4.421
	3	4							4.88	4.401
Di CBP			0.244	0.16		223	2.2	0.6		5.19
	4	2/2							5.35	5.023
	8	2/4	0.094						3.53	5.301
	15	4/4	0.15	0.16					2.34	5.335
Tri CBP			0.643	0.275		257	0.67	0.2		5.62
	5	26/2							3.88	5.481
	17	24/2	0.19	0.05					2.56	5.761
	18	25/2	0.13	0.11		257.5			1.69	5.551
	27	26/3							2.56	5.447
	29	245/		0.02					1.69	5.743
	31	25/4	0.24	0.05	*				1.69	5.677
	28	24/4	0.083	0.045					1.69	5.691
Tetra CBP			16.02	0.482		292	0.23	0.06		6.54
	47	24/24	0.17	0.11					1.23	6.291
	52	25/25	6.2	0.24					1.23	6.091
	49	24/25	1.1	0.06					1.23	6.221
	44	23/25	2.6	0.048					1.23	5.811
	74	245/4	0.92	0.03					0.81	6.671
	70	25/34	3.9	0.054					0.81	6.231
	66	24/34	1.3	0.05	*				0.81	5.452
	77	34/34	0.022	0.006	0.0005				0.28	6.523
Penta CBP			53.3	9.939		326	0.072	0.015		6.73
	95	236/25	11	4	*				0.89	6.137
	101	245/25	10	3.5					0.59	7.071
	99	245/24	3.5	0.12					0.59	7.211
	97	245/23	3	0.079					0.59	6.671
	87	234/25	4.8	0.39					0.59	6.371
	105	234/34	3.3	0.12	0.0001				0.59	6.657
	110	236/34	10	1.3	*				0.59	6.532
	114	2345/4			0.0005				0.39	6.657
	118	245/34	7.7	0.43	0.0001				0.39	7.121
	123	345/24	0.81		0.0001				0.39	6.747
	126	345/34	0.003		0.1				0.26	6.897
Hexa CBP			26.19	40.84		361	0.021	0.005		7.16
	151	2356/25	0.99	4.2					0.42	6.647
	149	2346/25	4.9	11					0.42	7.281
	153	245/245	5.1	11					0.28	7.751
	132	234/236	2.8	2.9					0.42	6.587
	137	2345/24	0.46	0.14					0.28	>7.711
	138	234/245	7.7	9.3	*				0.28	7.441
	158	2346/34	1.1	0.85					0.28	7.027
	128	234/234	1.7	0.49					0.28	6.961
	156	2345/34	1	0.45	0.0005				0.19	7.187
	157	234/345		0.14	0.0005				0.19	7.187
	167	245/345	0.21	0.21	0.00001				0.19	7.277
	169	345/345	0.23	0.16	0.01				0.12	7.427
Hepta CBP			3.09	38.27		395	0.006	(0.0015)		7.28
	187	2356/245	0.39	7.2					0.20	7.177
	183	2346/245	0.31	3.3					0.20	7.207
	174	2345/236	0.49	6.2					0.20	7.117
	177	235/2346	0.29	3.2					0.20	7.087
	180	2345/245	0.97	13	0.00001				0.13	7.367
	170	2345/234	0.64	5.2	0.0001				0.13	7.277
	189	2345/345		0.17	0.0001				0.09	7.717
Octa CBP			0.731	10.2		430	0.002	(0.0005)		7.88
	201	2346/2356	0.68	2.9					0.15	7.627
	203	23456/245	0.051	3.1					0.10	7.657
	195	23456/234		1.3					0.10	7.567
	194	2345/2345		2.9	*				0.06	8.683
Nona CBP			0	0.72		464	0.0007	(0.00015)		9.14
	207	23456/2346		0.05					0.07	7.747
	206	23456/2345		0.67					0.05	9.143
Deca CBP			0	0.05		499	0.0002	(0.00004)		9.6
	209	23456/23456		0.05					0.03	9.603
Sum			100.218	100.936						

MW, solubility, and v. pressure from Mackay et al., 1983; K$_{OW}$ from Eisler and Belisle, 1996;* = non-Ah toxicity,

TEF = toxic equivalencies from Eisler and Belisle, 1996; Gerstenberger et al., 1997; and Kannan et al., 1998; structure from Eisler and Belisle, 1996; Newman et al., 1998; parentheses indicate speculative values; Henry's Law, Brunner et al., 1990 est.

The pattern of chlorine substitution affects toxicity (Schweitzer et al., 1997) and also influences metabolism (biotransformation to other congeners) and thus bioaccumulation (Bright et al., 1995). The more toxic PCBs are the coplanar congeners that have zero or one Cl in the *ortho* position (Campfens and Mackay, 1997). The availability of adjacent unsubstituted carbons in *meta* and *para* positions facilitates metabolic transformation (Bright et al., 1995) and detoxification and excretion (Gutjahr-Gobell et al., 1999).

The Monsanto Company historically produced nine mixtures of PCBs known as Aroclors 1221, 1232, 1016, 1242, 1248, 1254, 1260, 1262, and 1268; the last two digits represent the percent Cl by mass, except for 1016, which has 41% Cl by mass (Newman et al., 1998). PCBs present in the Housatonic River appear to be predominantly Aroclor 1260, although Aroclors 1254 and 1242 were discharged as well (WESTON, 2000). Only approximately 75% of the 209 possible congeners were actually produced in the synthesis of the commercial Aroclor mixtures. Congener-specific analysis is important because of effects that have been linked to specific congeners (Gerstenberger et al., 1997; Van den Berg et al., 1998).

It is not feasible to model all congeners in this modeling effort because of the computational load. DiPinto and Coull (1997) found that in bioaccumulation studies classifying congeners according to K_{OW} was more useful than classifying them according to degree of chlorination; K_{OW} is a function of both the number and positioning of Cl on the PCB molecule. This methodology is also limiting because it can mask patterns of biotransformation. Therefore, a compromise is to model homologs, much as Thomann et al. (1991) did for the Hudson River, and to separately model some of the more toxic congeners (e.g., PCBs 77, 126, and 169).

CHEMICAL AND MICROBIAL DEGRADATION AND LOSS

Some congeners are dechlorinated selectively by either aerobic or anaerobic bacteria (Butcher et al., 1997). Only the heavier congeners are dechlorinated anaerobically, and only the lighter congeners are degraded aerobically (Jafvert and Rogers, 1990). Some methanogenic bacteria, which are anaerobic, dechlorinate PCBs at *meta* and *para* positions, enhancing Cl_1, Cl_2, and Cl_3 *ortho*-substituted PCBs, and counteracting selective enrichment of some congeners (Bright et al., 1995).

The rate of anaerobic dechlorination depends primarily on *meta* and *para* removal (Brown et al., 1984; Bedard and Quensen, 1995; Quensen et al., 1998; Sokol et al., 1998b). Different geographic sites exhibit different characteristic specificities for PCB dechlorination; at least seven distinct microbial dechlorination activities have been identified in Woods Pond (Wu et al., 1997a). Process P is restricted to removal of *para* chlorines with at least one adjacent chlorine; primarily homologs Cl_4 through Cl_7 are affected, with a large increase in congener 25/25, as has been noted in Woods Pond (Bedard and May, 1996).

This process has a temperature optimum at 20°C (Wu et al., 1996) and a range of 12 to 34°C (Wu et al., 1997b). Process N is restricted to removal of *meta* chlorines with at least one adjacent chlorine; nearly all Cl_6 and Cl_7 and many Cl_5 homologs in Aroclor 1260 are subject to this process, resulting in a large increase in congener 24/24, as noted in Woods Pond (Bedard and May, 1996). This process has a range of 8 to 30°C (Wu et al., 1997b). Van Dort and Bedard (1991) found *ortho* dechlorination of a congener; however, this process does not appear to be important in the field.

This process has a temperature optimum at 15 and 27 °C and a range of 8 to 30°C (Wu et al., 1996); it dominates at 15 °C (Wu et al., 1997b).

Bedard et al. (1997) stimulated a new unflanked *para* dechlorination activity, which they called Process LP; this process works in concert with Process N to further dechlorinate PCBs. Process LP has a temperature range of 18 to 30°C (Wu et al., 1997b). Overall, dechlorination of Aroclor 1260 occurs above 8°C, with optimal removal between 20 and 27°C (Wu and Wiegel, 1997). Temperatures in the top 45 cm of sediments in Woods Pond are 1 to 4 °C in winter, 8 to 12 °C in spring and fall, and 15 to 22 °C in summer (Wu et al., 1999).

Although disputed by some, Sokol et al. (1998b) found that removal is a function of PCB concentration and that dechlorination is effective only above a threshold concentration. Anaerobic transformation of highly chlorinated congeners into lower chlorinated congeners in a variable environment makes them subject to later aerobic microbial degradation, which can oxidatively mineralize lower Cl congeners, especially homologs Cl_1 and Cl_2, to carbon dioxide and water (Bedard et al., 1987; Bedard and Quensen, 1995; Gerstenberger et al., 1997; Sokol et al., 1998b). In one study, anaerobic dechlorination decreased total Cl by 36%; however, more than 33% of *meta* and *para* Cl remained after 39 months of anaerobic incubation (Sokol et al., 1998a). In another study, highly chlorinated congeners declined between 1988 and 1993 in an Ontario stream due to dechlorination by anaerobic bacteria (Zaranko et al., 1997). Anaerobic dechlorination has been coupled with aerobic biodegradation as a mechanism for bioremediation of PCBs (Abramowicz, 1994).

Volatilization can provide an important pathway for loss of PCBs. The lower chlorinated homologs in particular are subject to volatilization, as indicated by their higher vapor pressures and lower Henry's Law constants summarized in Table 1 (the Henry's Law constants currently are being estimated using HenryWin Ver. 3.02 with verification from the experimental literature). This can result in both a loss and source of the lighter homologs—a source because upon volatilization the atmosphere is enriched with these homologs, which are then subject to atmospheric deposition. PCBs, especially those that have been dechlorinated to Cl_1, Cl_2, and Cl_3, are very susceptible to volatilization upon drying; a maximum of 1.7% of PCBs were emitted per day in one experiment (Bushart et al., 1998). Another experiment, using very thin sediment layers, found even larger loss rates (Chiarenzelli et al., 1996).

Aside from volatilization and biotransformation by microbes and higher organisms, PCBs are remarkably stable. They are affected by neither hydrolysis nor oxidation. Atmospheric photodegradation has been shown to break down Cl_2 homologs, but higher chlorinated compounds are very resistant to this degradation pathway (Neely, 1983). In contrast, experiments with high-intensity UV lamps showed significant dechlorination of Cl_3 through Cl_7 congeners and accumulation of Cl_2 through Cl_4 congeners in soil; however, direct sunlight exposure gave no detectable response (IT Corp., 1999).

SORPTION AND DESORPTION TO ORGANIC MATTER AND BIOAVAILABILITY

Dissolved and particulate organic detritus are very important in controlling both the direct and dietary uptake of PCBs. Association of PCBs with colloidal and dissolved organic matter (DOM) reduces bioavailability; such contaminants are unavailable for uptake by organisms (Landrum et al., 1985, 1987; Stange and Swackhamer, 1994; Gilek et al. 1996; Butcher et al., 1998). Therefore, it is imperative that DOM and DOM complexation with PCBs be modeled correctly. Not all organic material is equal in sorptive affinity (Brannon et al., 1998).

Hydrophobic chemicals partition in nonpolar organic matter (Abbott et al., 1995). Humic acids exhibit high polarity. In one study, natural humic acids from a Finnish lake with extensive marshes were spiked with Cl_4-PCB, but a resulting PCB-humic acid complex could not be demonstrated (Maaret et al., 1992). In another study, Freidig et al. (1998) used artificially prepared Aldrich humic acid to determine a humic-acid DOC partition coefficient:

$$\log K_{DOC} = 0.67 \cdot \log K_{OW} + 1.46$$

This is, in turn, compared to the relationship reported by Koelmans and Heugens (1998) for partitioning to algal exudate:

$$\log K_{DOC} = 1.0 \cdot \log K_{OW} - 0.055$$

This strong association was found to limit availability to the living algae (Koelmans and Heugens, 1998). Nonpolar lipids in algae occur in the cell contents, and it is likely that they constitute part of the exudate, which may be both excreted and lysed material.

Association of PCBs with particulate organic matter (POM) also removes the PCBs from being available for direct uptake, but makes them available to the detrital food web, which is an important pathway in rivers such as the Housatonic. Again, there appears to be a dichotomy in partitioning, but in this case the literature suggests that it is the opposite of the pattern exhibited by DOM, in that labile POM does not take up PCBs as rapidly as refractory POM. Algal cell membranes contain polar lipids, and it is likely that this polarity is retained in the early stages of decomposition. The coefficient of partitioning of PCBs to particulate organic carbon (K_{POC}), does not remain the same upon aging, death, and decomposition, probably because of polarity changes. In an experiment using fresh and aged algal detritus, there was a 100% increase in K_{POC} with aging (Koelmans et al., 1995). K_{POC} increased as the C/N ratio increased, indicating that the material was becoming more refractory. In another study, K_{POC} doubled between day 2 and day 34, probably due to deeper penetration and lower polarity (Cornelissen et al., 1997).

Bioavailability depends on the type of dissolved and particulate organic matter in the system. Binding capacity of PCBs with POC is greater than that observed with DOC in Great Lakes waters (Gilek et al., 1996) (Stange and Swackhamer, 1994). In a study using Baltic Sea water, less than 7% of the PCBs were associated with DOC; most were associated with algae (Björk and Gilek, 1999).

In contrast, in a study using algal exudate and PCB 180 with log K_{OW} of 7.36, 98% of the dissolved concentration was as a DOC complex and only 2% was bioavailable (Koelmans and Heugens, 1998).

Unfortunately, older data and modeling efforts failed to distinguish between PCBs that were truly dissolved and those that were complexed with DOM. For example, the PCB water concentrations for Lake Ontario, reported by Oliver and Niimi (1988) and used by many subsequent researchers, included both dissolved and DOC-complexed PCBs (a fact that they recognized). In their steady-state model of PCBs in the Great Lakes, Thomann and Mueller (1983) defined "dissolved" as that which is not particulate (passing a 0.45-micron filter). In their Hudson River PCB model, Thomann et al. (1991) again used this operational definition of dissolved PCBs.

The structure of a PCB congener and its origin are also important in determining the fate in the detrital system. In deeper bodies of water, POM is often released as fecal pellets and sinks rapidly to the bottom sediments (Baker et al. 1991). Cl_2 to Cl_4 homologs may be present in higher concentrations in fecal material, but they are also released quickly (Baker et al., 1991). Planar PCBs bind strongly to POM and are less bioavailable (van Bavel et al. 1996). Highly chlorinated homologs sorb strongly to POM and are not assimilated easily by detritus feeders (Boese et al., 1995).

BIOACCUMULATION AND BIOTRANSFORMATION

General Principles

Several early bioaccumulation models used the concept of a food-chain multiplier, which is now considered excessively simplistic (Campfens and Mackay, 1997). Food-web modeling is now considered necessary except for screening level studies (Abbott et al., 1995). The best way to assess bioaccumulation accurately is to use more complex models, but only if the data needs of the models can be met and there is sufficient time (Pelka, 1998). "Food web models provide a means for validation because they mechanistically describe the bioaccumulation process and ascribe causality to observed relationships between biota and sediment or water" (Connolly and Glaser, 1998).

Often there is an absence of equilibrium, especially in fish, due to insufficient exposure time or organism growth, metabolic biotransformation, dietary exposure, and nonlinear relationships for very large and/or superhydrophobic compounds (Bertelsen et al., 1998). Although it is important to have a knowledge of equilibrium partitioning because it is an indication of the condition toward which systems tend (Bertelsen et al.,1998), it is often impossible to determine steady-state potential due to changes in bioavailability and physiology (Landrum, 1998). PCBs may not be at steady state even in large systems such as Lake Ontario that have been polluted over a long period of time. In fact, PCBs in Lake Ontario exhibit a 25-fold disequilibrium (Cook and Burkhard, 1998). The challenge is to obtain sufficient data for a kinetic model (Gobas et al., 1995).

Accumulation from sediment in plankton and fish is largely determined by degree of chlorination, which affects both surface sorption and partitioning. Maximum bioaccumulation occurs for Cl_5, Cl_6, and Cl_7 congeners; Cl_3 and Cl_4 congeners are depleted due to low lipophilicity; Cl_8 congeners are depleted due to size or steric effects (Willman et al., 1997). Plankton and fish are enriched in high-K_{OW} congeners and depleted in low-K_{OW} congeners; there is a systematic enrichment of Cl_5, Cl_6, and

Cl$_7$ congeners and depletion in Cl$_3$ congeners with increasing trophic level (Oliver & Niimi, 1988; Campfens and Mackay, 1997; DiPinto and Coull, 1997).

Within homolog groups, congeners with less *ortho*-substitution have greater K$_{OW}$ values and are accumulated up the food chain at a greater rate than other congeners in their homolog group. Changes in distributions of congeners mainly are caused by transfers among biotic compartments (Campfens and Mackay, 1997). There is no enrichment of mono- and non-*ortho*-substituted congeners with an increase in trophic level. However, many coplanar congeners, especially the more toxic PCB 77, are depleted with increasing trophic level; PCB 77 is almost certainly metabolized (Campfens and Mackay, 1997).

Algae (Periphyton and Phytoplankton)

Bioaccumulation of PCBs in algae is dependent on solubility, hydrophobicity and molecular configuration of the congener, and growth rate, surface area and type, and content and type of lipid in the algae (Stange and Swackhamer, 1994). Phytoplankton biomass may double or triple in 1 day and periphyton turnover may be so rapid that some PCBs will not reach equilibrium (Hill and Napolitano, 1997); therefore, one should use the term "bioaccumulation factor" (BAF) for plants as well as animals rather than "bioconcentration factor," which implies equilibrium (Stange and Swackhamer, 1994).

PCBs partition to lipids in algae, but the relationship is not a simple one. In phytoplankton, lipids can range from 3 to 30% by weight (Swackhamer and Skoglund, 1991). However, not all lipids are the same. Polar phospholipids occur on the surface. PCBs preferentially partition to internal neutral lipids, but those are usually a minor fraction of the total lipids, and they vary depending on growth conditions and species (Stange and Swackhamer, 1994). Algal lipids have a much stronger affinity for PCBs than does octanol, so that the algal BAF$_{lipid}$ > K$_{OW}$ (Stange and Swackhamer, 1994; Koelmans et al., 1995; Sijm et al., 1998).

There is probably a two-step bioaccumulation mechanism for PCBs to algae, with rapid surface sorption of 40 to 90% within 24 hours and then a small, steady increase with transfer to interior lipids for the duration of the exposure (Swackhamer and Skoglund, 1991). Uptake increases with increase in the surface area of algae (Wang et al., 1997). Therefore, the smaller the organism the larger the uptake rate constant (Sijm et al., 1998). However, in small phytoplankton, such as the nannoplankton that dominate the Great Lakes, although a high surface-to-volume ratio can increase sorption, high growth rates can limit PCB concentrations (Swackhamer and Skoglund, 1991). The combination of lipid content, surface area, and growth rate results in species differences in BAF among algae (Wood et al., 1997).

The pattern of bioaccumulation to algae varies among PCB homologs: Cl$_2$-Cl$_5$ have favorable steric factors but low BAFs; Cl$_5$-Cl$_7$ have favorable BAFs, some have favorable steric factors and high BAFs, others have low steric factors and low BAFs; Cl$_7$ - Cl$_{10}$ have high K$_{OW}$s, but poor steric factors, so low BAFs (Stange and Swackhamer, 1994). Highly chlorinated congeners are associated with cell membranes (phospholipids) (Stange and Swackhamer, 1994). There is no direct relationship between BAF and K$_{OW}$ for log K$_{OW}$ > 7 (Swackhamer and Skoglund, 1991).

Desorption is significantly slower than sorption (Swackhamer and Skoglund, 1991). Depuration from algae is very slow (Zaranko et al., 1997). Elimination is not just a function of physicochemical properties, but is assumed to be dependent on exudation (Koelmans and Heugens, 1998; Sijm et al., 1998). It has been noted that sorption to algal exudates decreases bioavailability and, in many studies, has resulted in underestimation of uptake rate constants and BAFs (Sijm et al., 1998). Algae lack enzymes for dechlorinating PCBs (Hill and Napolitano, 1997), and no metabolism of PCBs has been reported for algae.

Macrophytes

Gobas et al. (1991) conducted uptake and elimination experiments with PCBs and other chemicals using the common aquatic weed *Myriophyllum spicatum,* and developed a kinetic model that fit the observed data well.

Invertebrates (Zoobenthos and Zooplankton)

Invertebrates are a critical link in both detrital and phytoplankton food webs. Higher molecular weight and more hydrophobic compounds are incorporated into sediments and are recycled by the zoobenthos (Baker et al., 1991). Lower weight, lower hydrophobicity compounds tend to be dissolved (Wood et al,. 1997), and their uptake is enhanced in filter feeders through sorption to phytoplankton (Gilek et al., 1996).

The partitioning between sediment carbon and lipids in zoobenthos is referred to as the biota sediment accumulation factor (BSAF, cf. Boese et al., 1995):

$$BSAF = \frac{tissue\ conc/tissue\ lipid}{sed\ conc/sed\ TOC}$$

Uptake of PCBs by benthic organisms is rapid (Zaranko et al., 1997). Ingestion rates in deposit feeders can be greater than 100 times body weight/day (Forbes et al., 1998), and they feed selectively on fine organic matter, which tends to have higher PCB concentrations (Boese et al., 1995, 1996). *Diporeia*, a common freshwater amphipod, feeds on particles from 20 to 63 microns in size (Wood et al., 1997); tubificids, which often dominate more polluted habitats, feed selectively on sediments with high organic matter; chironomids (common midge larvae) are grazers of algae and gatherers of detritus (Zaranko et al., 1997).

Much attention has been given to the role of pore water in the uptake of PCBs by benthos. However, "it may be unwise to uncritically assume that pore-water contaminant is the most bioavailable." Many animal burrows are lined, and the composition of the water in burrows is equivalent to that of the overlying water (Forbes et al., 1998). Campfens and Mackay (1997) found that predicted PCB concentrations in benthos exceeded those measured for high-K_{OW} congeners, possibly due to assumptions regarding the respiration of pore water. Uptake of very hydrophobic compounds from sediment was observed to be one to five times greater than that predicted by equilibrium partitioning

from pore water (Loonen et al., 1997)—clearly the important pathway of exposure is through the ingested detritus.

Bioaccumulation of lighter homologs may reflect direct uptake from water (Bright et al., 1995). The exposure of filter feeders to the overlying water is quite different from that of deposit feeders. The pumping rate of mussels is 100 times greater than that of a deposit-feeding clam; however, this is offset somewhat by decreased efficiency of uptake at higher pumping rates (Björk and Gilek, 1999).

Optimum bioaccumulation in invertebrates occurs with homologs Cl_5 to Cl_7; homologs $< Cl_5$ have reduced partition values, and those $> Cl_7$ have an unfavorable steric (size) effect (Wood et al., 1997). A parabolic relationship was observed between *Mytilus* log BAF and log K_{OW} (Gilek et al., 1996). Bioavailability declines with increasing hydrophobicity in Cl_7-Cl_{10} homologs, and there is a negative relationship for BSAF and log K_{OW} (Maruya and Lee, 1998). In *Macoma nasuta* there was an observed reduction in uptake with increasing K_{OW}, possibly due to reduced desorption rates from sediment, increasing steric hindrance, and reduced translocation to lipid pools (Boese et al., 1997). As a result, many experiments with highly chlorinated congeners do not reach steady state; for example, uptake of Cl_8 did not reach steady state in *M. nasuta* in 30 days (Boese et al., 1995). *M. nasuta* uptake efficiency for Cl_{10} was 0% (Kannan et al., 1998).

The longevity of homologs in sediments reflects in part the uptake or lack of uptake by invertebrates. For example, in one study, CL_9 predominated in sediments (Kannan et al., 1998). In an experiment by Boese et al. (1995) with deposit feeders, Cl_3 through Cl_6 declined significantly in spiked sediments over 30 days.

The quantitative relationships of dietary uptake have been quantified by several authors. In one modeling study, gut absorption efficiency was computed by an empirical relationship with a maximum of 0.43 (Campfens and Mackay, 1997). Data on uptake by small fish published by Gobas et al. (1993) suggest a mean of 0.63, with no trend in efficiency between log K_{OW} 4.5 and 7.5 (although that was not their conclusion). Nichols et al. (1998) demonstrated that uptake is more efficient in larger fish, with a mean of about 0.90. Invertebrates generally exhibit lower efficiencies; Landrum and Robbins (1990) showed that values ranged from 0.42 to 0.24 for chemicals with log K_{OW}s from 4.4 to 6.7. Assimilation efficiencies of PCB congeners from algae were determined for *Mytilus edulis*: 0.1 to 0.5 for PCB 31, 0.1 to 0.7 for PCB 49, and 0.2 to 0.7 for PCB 153 (log K_{OW} = 7.751). PCB 153 assimilation efficiency was measured as 0.69 for zebra mussels; the formation of pseudofeces (rejected food) in the presence of high algal concentrations could have caused underestimation of the *M. edulis* assimilation efficiencies (Björk and Gilek, 1999).

M. edulis gill assimilation efficiencies from water were 0.1-0.2 for PCB 31, 0.1-0.4 for PCB 49, and 0.3-0.6 for PCB 153 (Björk and Gilek, 1999). *Macoma nasuta*, a deposit feeder, had an uptake efficiency of 0.82 (Björk and Gilek, 1999). Gill assimilation efficiencies decline with an increased ventilation rate because of diffusional dead space and decreased contact time between gills and water (Björk and Gilek, 1999).

No relationship was found between depuration and K_{OW} (Boese et al., 1997). For reasons that are not understood, PCBs accumulated from water are retained longer than those obtained from food (Wang, 1998). Biotransformation of Cl_3 is rapid in *M. nasuta* (Boese et al., 1995). Chironomid

larvae retained 97.8% of Aroclor 1242 after 7 days (Wang, 1998). Generally, non-*ortho*-substituted congeners are stable in invertebrates (Bright et al., 1995). Coplanar PCBs biomagnify and achieve steady state in *Mytilus* faster than nonplanar PCBs (Bergen et al., 1996). More detailed structural activity relationships can be elucidated (for example, Wood et al. [1997]), but they are very specific and are beyond the scope of this application.

Fish

Bioaccumulation of PCBs in fish is of concern because of risks to fish, wildlife, and humans. Hydrophobic contaminants such as PCBs accumulate in fish with both increasing age, size, and position in the food web. Stow and Carpenter (1994) found that age is a better predictor of PCBs than size in Lake Michigan salmon.

There are several published K_{OW}-BCF models; in all, the intercept terms are negative because limited accumulation in tissues other than lipid reduces concentrations expressed on a whole-fish basis (Bertelsen et al., 1998). Unlike algae, there is no theoretical basis for a K_{OW}-lipid coefficient for fish other than 1.0. In a study by Bertelsen et al. (1998), 90% of variance in the data was accounted for by the combined model of log K_{OW} and total lipid:

$$\log\ (K_{tw} - \textit{Waterfrac}) = 0.74 \cdot \log K_{OW} + 1.00 \cdot \log \textit{Lipidfrac} + 0.72$$

where:
K_{tw}	=	tissue-water partition coefficient;
Waterfrac	=	water content (fraction); and
Lipidfrac	=	lipid fraction.

Lipid fraction is quite variable among species and even in the same species over the course of a year or lifetime. Lipid concentrations in fish have been documented to range from 2 to 27.6% (Sijm and van der Linde, 1995; Zaranko et al., 1997; Gerstenberger et al., 1997). Fathead minnows have been observed to have post-spawning reductions in lipid content of as much as 72% in males and 46% in females due to breeding activities, including cleaning and defense of nests as well as egg laying (Suedel et al., 1997).

Uptake kinetics are important for representing the short-term exposures associated with storm events and accidental spills. There are two pathways for direct uptake: through the gills and through the skin. Bioconcentration has been modeled over the last decade as diffusion through aqueous and lipid layers (Gobas and Mackay, 1987; Barber et al., 1988; Erickson and McKim, 1990; Sijm and van der Linde, 1995). The uptake rate constant k_1 increases with K_{OW} up to log K_{OW} 3, is constant between log K_{OW} 3 and 6, then decreases with log $K_{OW} > 6$ (McKim et al., 1985); resistance changes from lipid to aqueous at log $K_{OW} \approx 3$ (Sijm and van der Linde, 1995). PCBs with 4 or fewer Cl atoms are most readily sorbed through the gills (Gerstenberger et al., 1997). Gill exposure is a function of respiration rate, decreasing in larger fish (Thomann and Mueller, 1987).

Dermal uptake can be significant for benthic feeders such as bullhead, which forage in sediments for aquatic organisms (Leadley et al., 1998). Juvenile spot fed copepods in contaminated sediment accumulated 4.83 times more PCBs as fish fed in clean sediment; exposure was through both skin and gills (DiPinto and Coull, 1997).

Dietary uptake may vary with molecular weight of the chemical, size of the predator, and the nature of the food. The literature differs on the importance of the K_{OW}. In pike fed spiked rainbow trout there was no dependency of dietary uptake efficiency on K_{OW}, but uptake efficiency did vary with molecular weight. Uptake efficiency was observed to be greatest at a molecular weight of ~450, which may be due to the structure of the membrane proteins; mediated uptake of pollutants associated with proteins has been suggested (Burreau et al., 1997). Gobas et al. (1988) found that uptake efficiency was constant up to log $K_{OW} = 7$ (discussed above with regard to invertebrates). In brook trout (150 g mean weight) net gut uptake efficiencies were >80%, compared to juvenile (5 to 9 g) rainbow trout and whitefish, with 43-58% and 66-76% uptake efficiencies, respectively. If changes occur with growth then this suggests that a single PCB uptake coefficient optimized for subadults would overestimate for juveniles (Nichols et al., 1988). Dietary composition can affect the uptake of PCBs, as shown by experiments with channel catfish (NIEHS, 1999).

Both depuration and, for some congeners, biotransformation can be important pathways for elimination of PCBs in fish. Depuration in juvenile trout exhibits a curvilinear relationship with log K_{OW}, apparently decreasing beyond log $K_{OW} = 7$, perhaps because equilibrium is not attained among compartments in the fish (Fisk et al., 1998). Lipid content and size are important for determining the elimination rate constant. Much lower depuration rates (and hence higher half-lives) occur in larger and/or fatter fish; for example, the half-life of a Cl_4 PCB in a 0.1-g guppy is 43 days, compared to 5.6 years in a 900-g rainbow trout (Sijm and van der Linde, 1995). Elimination may occur across the skin as well as through the gills, increasing in small fish with large surface area-to-volume ratios (Sijm and van der Linde, 1995).

Metabolic transformation increases the elimination rate. Biotransformation has the greatest effect on hydrophobic compounds where excretion approaches zero; limited accumulation of lower chlorine homologs may be due in part to biotransformation (Endicott and Cook, 1994). Fish are known to metabolize certain congeners, namely PCBs 101, 105, 107, 110, 138, and 170 (Hill and Napolitano, 1997); primarily these are planar congeners, which are toxic. Few fish show enzyme induction that would suggest lower Cl congeners are metabolized (Gerstenberger et al., 1997). In fact, this may account for the bioaccumulation of lighter Cl congeners in salmonids (Bright et al., 1995).

Migratory behavior of fish can be important in determining their exposure. For example, minnows migrate during early spring and fall; PCB concentrations in minnows in an Ontario stream varied seasonally with the lowest concentration in October (Zaranko et al., 1997). Likewise, migration of striped bass in the Hudson estuary is significant and contributes to the observed variability in PCBs (Thomann and Farley, 1998). In contrast, largemouth bass are known to be territorial and tend to stay in their home areas (Parker and Hasler, 1959).

Birds

PCB concentrations in mallards have been reported to be highly correlated with exposure (Cobb et al., 1997) and exposure of mallards and wood ducks to PCBs has been documented in the Housatonic River. Studies on tree swallows, which feed on emergent insects, have shown that total PCB values in eggs and nestlings may attain near-steady-state and that enrichment of Ah-active congeners occurs while other congeners are dechlorinated (Froese et al., 1998). Planar PCB congeners (77 and 126) are very toxic to hatching chicken embryos (Hoffman et al., 1998). Young of all bird species in the Green Bay, Wisconsin, area accumulated the toxic congeners PCBs 77, 105, 126, and 169 (Ankley et al., 1993).

A relatively simple two-compartment model representing the partitioning between fat and blood plasma in gulls was shown to describe the concentration dynamics (Clark et al., 1988).

Mammals

Piscivorous mammals are exposed to high levels of pollutants due to feeding at the top of aquatic food webs (Bremle et al., 1997). Variation in the rate of bioaccumulation of different congeners may be due to steric factors that affect the binding energy of a substrate (Bright et al., 1995). In general, higher-chlorinated PCBs have higher BAFs than lower-chlorinated PCBs. Congeners lacking Cl in the *meta* and *para* positions exhibit low BAFs; in many mammals these are hydroxylated and excreted (Bright et al., 1995; van Bavel et al., 1996).

Reduction in birth rate and weights have been observed in several studies of mink fed PCB-contaminated food (Russell et al., 1997; Halbrook et al., 1999). A preferential enrichment of dioxin-like congeners PCBs 126 and 169 occurs from fish to otters; these toxic compounds are retained in the liver (Leonards et al., 1997). PCB 77, another toxic congener, appears to be metabolized in otters (Leonards et al., 1997). A model developed by Traas et al. (in press) simulates bioaccumulation and toxicity of dioxin-like congeners in otters. Sample and Suter (1999) used @RISK to model the effects of PCBs on otter, mink, heron, and osprey in Poplar Creek and Clinch River, Tennessee.

TOXICITY

Although the toxicity of PCBs was briefly mentioned in the previous section on bioaccumulation, a more detailed discussion is provided below. Few PCB congeners exhibit acute toxicity (Bright et al., 1995), but exposure may result in chronic effects, adversely affecting survival, growth, and reproduction (Suedel et al., 1997). Because of congener-specific toxicities, total body burden of PCBs is inadequate for predicting effects (Schweitzer et al., 1997). Acute toxicity is demonstrated by non-*ortho*-substituted planar congeners similar to dioxins; these dioxin-like congeners also exhibit chronic toxicity (Bergen et al., 1996), including wasting disease (Suedel et al., 1997). The non-*ortho*-substituted PCBs assume a planar configuration and have a high affinity for the dioxin (Ah) receptor (Bright et al., 1995; Campfens and Mackay, 1997). The planar congeners PCBs 77, 126, and 169 have been demonstrated to date to be the most toxic congeners in fish and mammals (Campfens and Mackay, 1997). Dioxin-like compounds have additive toxicity (Suedel et al., 1997; Elonen et al., 1998). It is common to express the toxicities as toxic equivalency factors (TEFs)

relative to the toxic potency of 2,3,7,8, tetradibenzodioxin (for example, Kannan et al., 1998; Traas et al., in press). The mammalian, fish and bird TEFs are summarized in Table 2.

In contrast, *ortho*-substituted congeners have a low affinity for the Ah receptor and may exhibit low toxicity—even insignificant sublethal effects (Suedel et al., 1997). However, exposure to some di-*ortho* congeners (including PCBs 138, 153, 180, and 194) produce adverse effects (carcinogenicity, neurotoxicity, and endocrine disruption) (Kannan et al., 1998). Other congeners that are not dioxin-like include PCBs 28+31, 47+48, 66+95 (pairs that are analytically indistinguishable) and PCBs 110, which have also been shown to be toxic in lab animals (Gerstenberger et al., 1997).

Information concerning toxicity of PCB metabolites is scarce; in general, metabolites of PCBs are considered to be less toxic than their parent compounds. However, it has been demonstrated that hydroxylated metabolites of PCB 77 bind competitively and are retained persistently in blood (Klasson-Wehler et al., 1998).

In a study with an estuarine minnow, reduced feeding and reduction in growth occurred in fish fed medium and high doses of PCBs. The bioaccumulation of congeners was proportional to that observed in fish collected in the field, except for PCB 77, which may have been metabolized (Gutjahr-Gobell et al., 1999). In another study, fecundity was reduced in association with the reduction in growth; egg production was reduced by 77% at the highest dose (part of which was due to 58% mortality) (Black et al., 1998a). This relationship was not found in the field, suggesting differences in exposure routes (Black et al., 1998b). In addition, it has been shown that Aroclor 1260 can alter sex ratios in trout at environmental concentrations (Matta et al., 1998).

Table 2

World Health Organization Toxic Equivalency Factors
(van den Berg et al., 1998)

Congener	Human/Mammals	Fish	Birds
2,3,7,8-TetraCDD	1	1	1
1,2,3,7,8-PentaCDD	1	1	1[b]
1,2,3,4,7,8-HexaCDD	0.1[a]	0.5	0.05[b]
1,2,3,6,7,8-HexaCDD	0.1[a]	0.01	0.01[b]
1,2,3,7,8,9-HexaCDD	0.1[a]	0.01[c]	0.1[b]
1,2,3,4,6,7,8-HeptaCDD	0.01	0.001	<0.001[b]
OctaCDD	0.0001[a]	<0.0001	0.0001
2,3,7,8-TetraCDF	0.1	0.05	1[b]
1,2,3,7,8-PentaCDF	0.05	0.05	0.1[b]
2,3,4,7,8-PentaCDF	0.5	0.5	1[b]
1,2,3,4,7,8-HexaCDF	0.1	0.1	0.1[b,d]
1,2,3,6,7,8-HexaCDF	0.1	0.1[d]	0.1[b,d]
1,2,3,7,8,9-HexaCDF	0.1[a]	0.1[c,d]	0.1[d]
2,3,4, 6,7,8-HexaCDF	0.1[a]	0.1[d,e]	0.1[d]
1,2,3,4,6,7,8-HeptaCDF	0.01[e]	0.01[e]	0.01[e]
1,2,3,4,7,8,9-HeptaCDF	0.01[e]	0.01[c,e]	0.01[e]
OctaCDF	0.0001[a]	<0.0001[c,e]	0.0001[e]
3,4,4',5-TetraCB(81)	0.0001[a,c,d,e]	0.0005	0.1[c]
3,3',4,4'-TetraCB(77)	0.0001	0.0001	0.05
3,3',4,4',5-PentaCB(126)	0.1	0.005	0.1
3,3',4,4',5,5'-HexaCB (169)	0.01	0.00005	0.001
2,3,3',4,4'-PentaCB(105)	0.0001	<0.000005	0.0001
2,3,4,4',5-PentaCB (114)	0.0005[a,d,e,f]	<0.000005[e]	0.0001[g]
2,3',4,4',5-PentaCB(118)	0.0001	<0.000005	0.00001
2',3,4,4',5-PentaCB(123)	0.0001[a,d,f]	<0.000005[e]	0.00001[g]
2,3,3',4,4',5-HexaCB (156)	0.0005[d,e]	<0.000005	0.0001
2,3,3',4,4',5'-HexaCB (157)	0.0005[d,e,f]	<0.000005[d,e]	0.0001
2,3',4,4',5,5'-HexaCB (167)	0.00001[a,f]	<0.000005[c]	0.00001[g]
2,3,3',4,4',5,5'-HeptaCB (189)	0.0001[a,d]	<0.000005	0.00001[g]

Abbreviations: CDD, chlorinated dihenzodioxins; CDF, chlorinated denzofurans; CR chlorinated biphenyls;
QSAR, quantitative structure-activity relationship.

[a] Limited data set.
[b] In vivo CYP1A induction after in ovo exposure.
[c] In vitra CYP1A induction.
[d] QSAR modeling prediction from CYP1A induction (monkey, pig, chicken, or fish).
[e] Structural similarity.
[f] No new data from 1993 review.
[g] QSAR modeling prediction from class-specific TEFs.

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